Joint Development and Coordination of Emissions Control Data and Models (CLEERS Analysis & Coordination)
Project ID: ACE022

Oak Ridge National Laboratory
National Transportation Research Center

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2020 U.S. DOE Vehicle Technologies Office
Annual Merit Review

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  - Haiying Chen
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  - Wei Li, Christine Lambert, Craig Dimaggio, Mike Cunningham, John Kirwan, Louise Olsson, Mike Harold
- **Collaboration with partners at PNNL:**
  - Ken Rappé, Mark Stewart, Yong Wang

ORNL Team Members

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Website

CLEERS Analysis Team

Sreshtha Sinha Majumdar

Passive NOx Adsorber Experiments & Mechanisms

Austin Ladshaw

NH_3 SCR Modeling

Calvin Thomas

Hydrocarbon Trap Experiments & Modeling

Overview

Timeline

Project start date: FY2019

Project end date: FY2021

- part of ORNL response to 2018 VTO "Lab Call"
- core activity since FY2000
- supports and coordinates emissions control research
- evolves with DOE priorities and industry needs

Budget

	FY19	FY20
Coordination	$250k	$250k
Analysis	$350k	$450k

Barriers

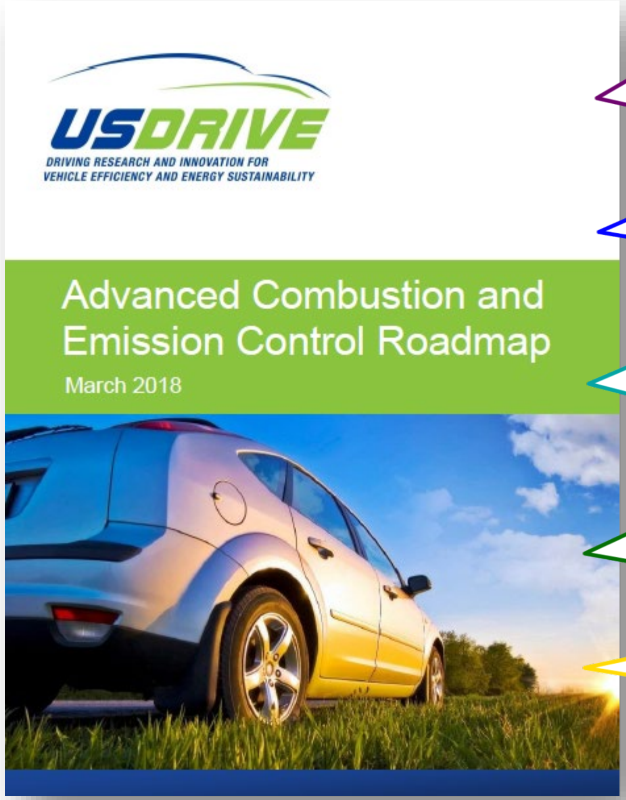
U.S. DRIVE Advanced Combustion & Emission Control 2018 Roadmap Barriers & Targets:

- U.S. EPA Tier 3 Bin 30 emission standard
- 90% conversion of criteria pollutants (NOx, CO, HCs) at 150°C for the full useful life of the vehicle
- "Development of models and simulation tools… to predict performance and better understand catalytic processes"

Partners

- DOE Advanced Engine Crosscut Team
- University of Virginia, Johnson Matthey, PNNL
- U.S.DRIVE ACEC Tech Team
- CLEERS Focus Group members:
  - 10 engine/vehicle manufacturers
  - 9 component and software suppliers
  - 12 universities
  - 4 national labs

U.S. DRIVE ACEC Roadmap and 21st Century Truck Research Blueprint both emphasize the need for advanced aftertreatment research to ensure emissions compliance for high efficiency combustion engines



"Compliance with exhaust emission regulations will be mandated and requires aftertreatment technologies integrated with the engine combustion approaches."

"The overarching emissions goal… is the U.S. EPA Tier 3 Bin 30 emission standard…"

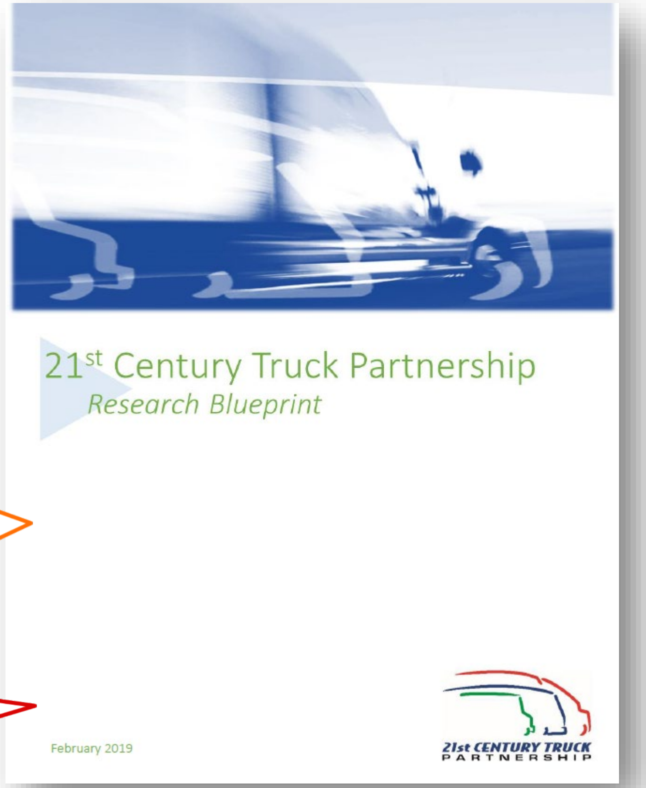
"…achieve greater than 90% conversion of criteria pollutants (NOx, CO, HCs) at 150°C for the full useful life of the vehicle."

"…development of models and simulation tools ranging from the molecular level to the system level to predict performance and better understand catalytic processes"

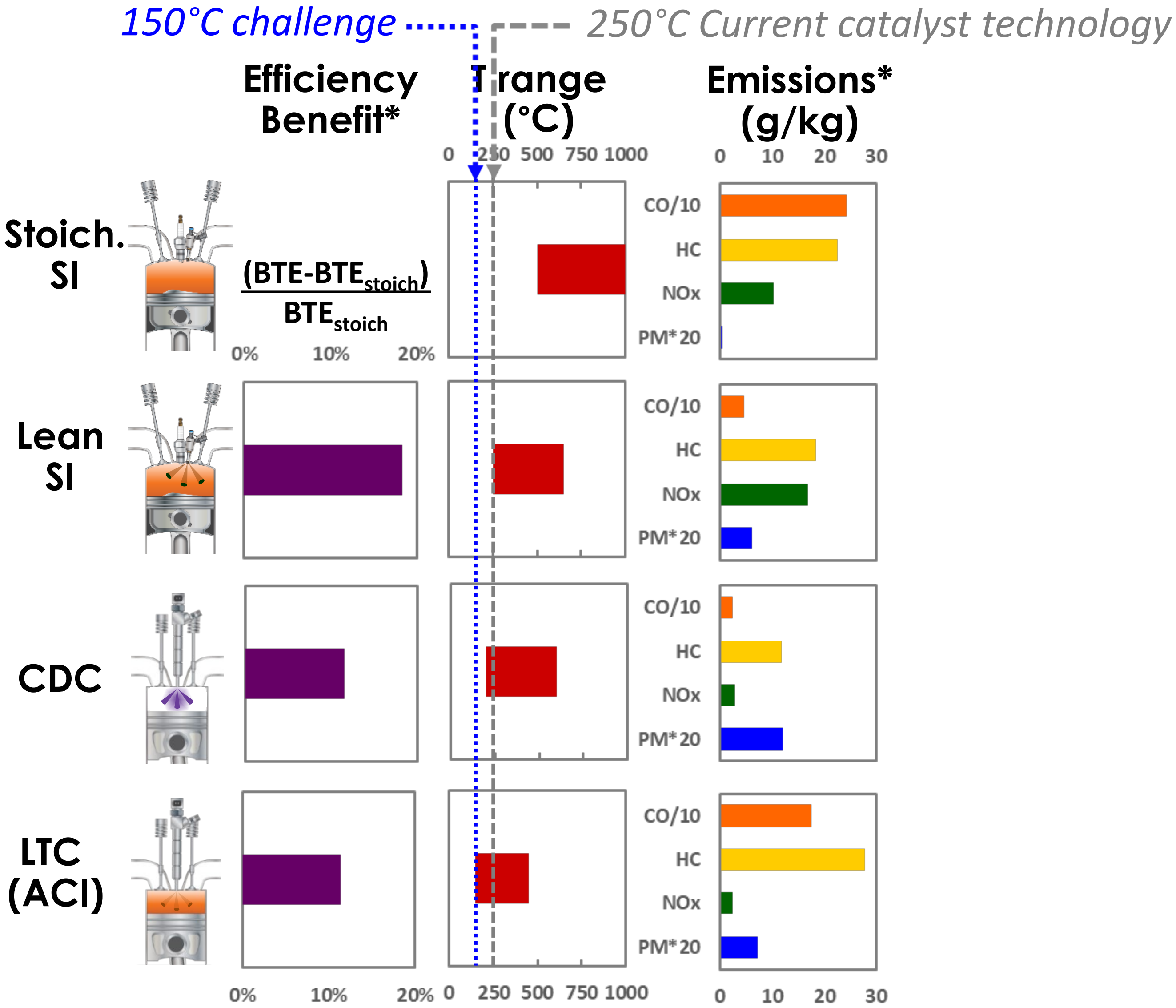
"Characterize and understand PNA/HC Trap durability"

"Innovations in catalyst materials and emission control systems, especially effective at low exhaust temperatures, are needed to greatly reduce the cost and ensure energy penalties are negligible."

"50% emissions reduction (below current standard) at 50% lower cost for the aftertreatment system"



Advanced combustion technologies improve efficiency, but lean low temperature exhaust creates emissions challenges that must be addressed before commercialization



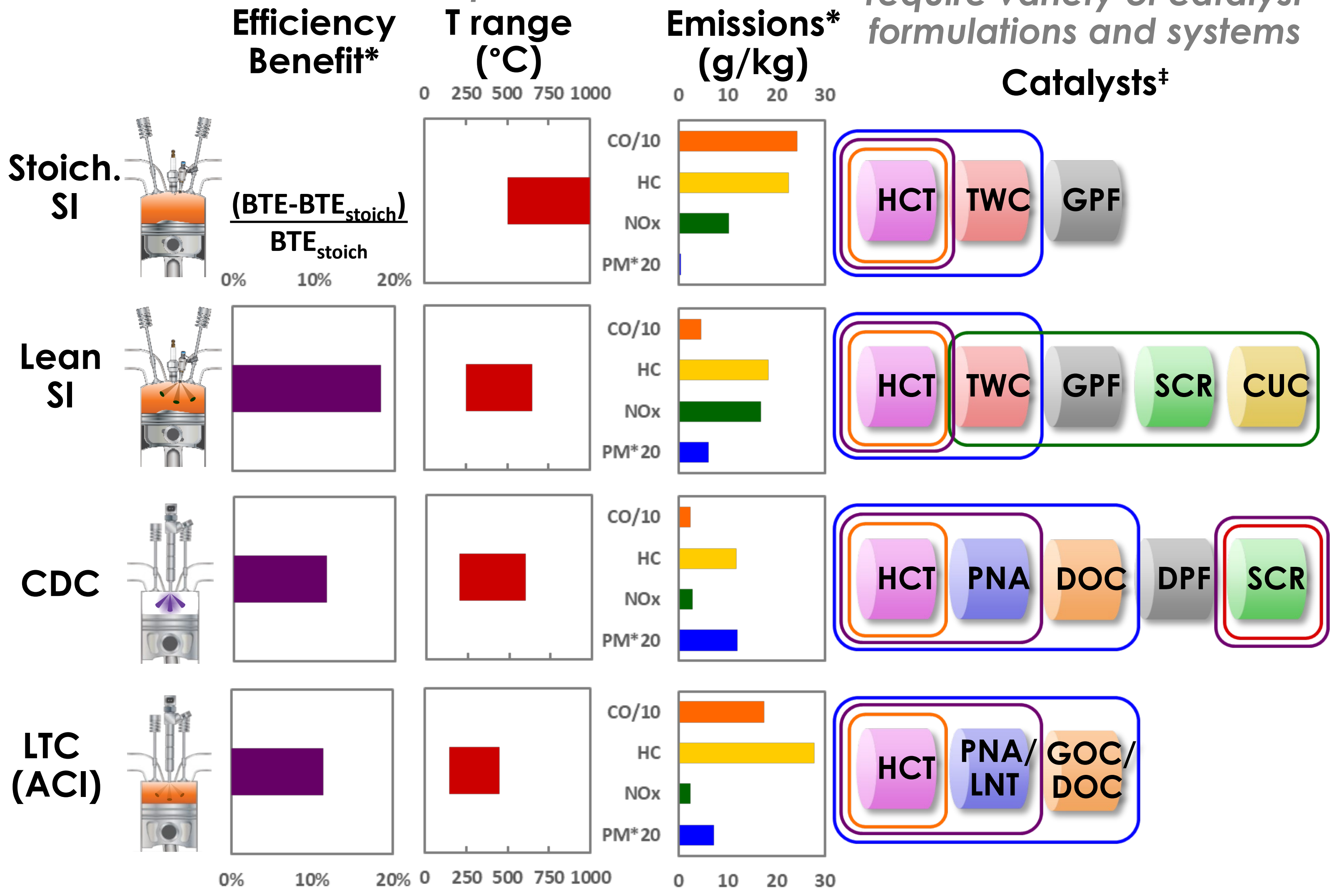
*(efficiency and emissions at 2000 rpm, ~2 bar BMEP)

Advanced combustion technologies improve efficiency, but lean low temperature exhaust creates emissions challenges that must be addressed before commercialization

Higher fuel efficiency = lower exhaust temperatures

Unique emissions profiles require variety of catalyst formulations and systems

ORNL R&D portfolio spans wide range of applications, technologies, size scales, commercial readiness



Projects

CLEERS (ACE022)
Model new trap materials and aging effects on SCR catalysts

Low Temperature Emissions Control (ACE085)
Discover new low T catalysts & traps

Lean Gasoline Emissions Control (ACE033)
Develop pathways for lean gasoline engines to meet emissions with minimum fuel penalty

Chemistry & Control of Cold Start Emissions (ACE153)
Understand how exhaust chemistry impacts device performance & design

Cummins Emissions Control CRADA (ACE032)
Understand how aging affects properties and performance of SCR catalysts

*(efficiency and emissions at 2000 rpm, ~2 bar BMEP)

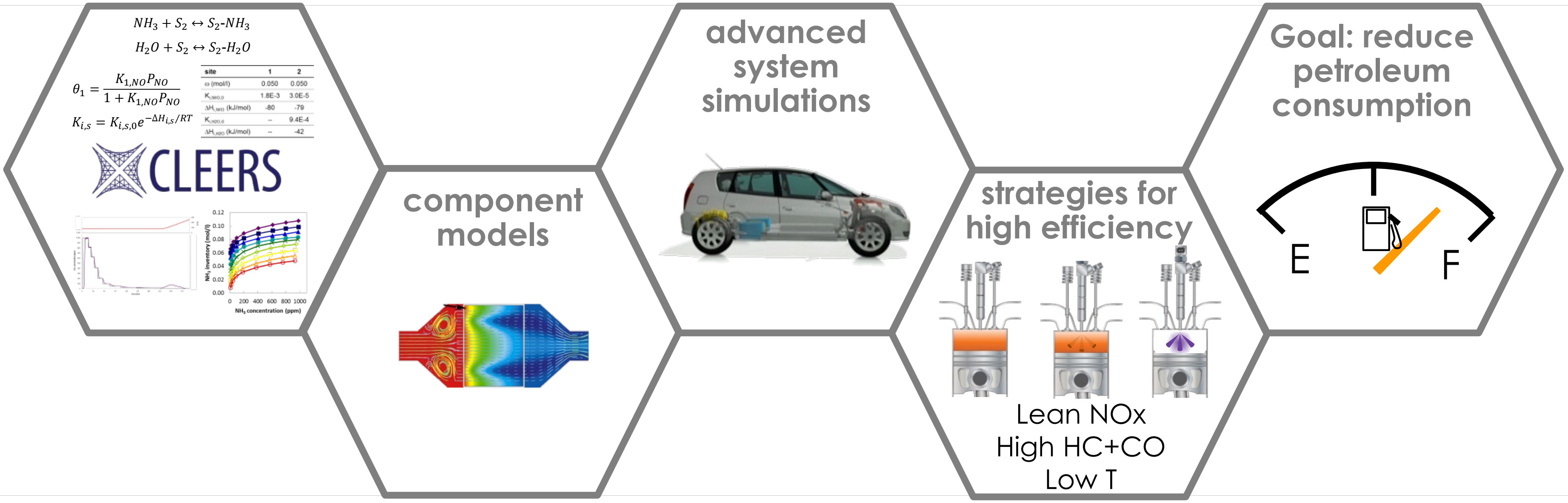
‡Abbreviations in backup slides

CLEERS provides a key stepping stone on the path to reduced petroleum consumption

- CLEERS = **C**rosscut **L**ean (/**L**ow-temperature) **E**xhaust **E**missions **R**eduction **S**imulations

- Mission: accelerate development of emissions control technologies for high efficiency advanced combustion engines by improving accuracy of aftertreatment system simulations

- Objectives:
  - develop and disseminate pre-competitive data, parameters, and models
  - support collaborations among industry, university, national lab partners
  - gather feedback from industry on critical emissions control research needs
  - coordinate DOE National Laboratory research efforts



ORNL coordinates CLEERS activities and conducts focused R&D in support of CLEERS objectives

ORNL CLEERS Coordination | **ORNL CLEERS Analysis**

Flow reactor experiments*
catalyst property measurements
protocol development
calibration & validation data sets

Specialized diagnostics
in situ DRIFTS
Spaci-MS, Spaci-IR

Characterization
microscopy
XRD
BET
chemisorption

Analysis
thermodynamics
parameter estimation

Modeling
micro-kinetic, global
Chemkin, Autonomie
custom codes

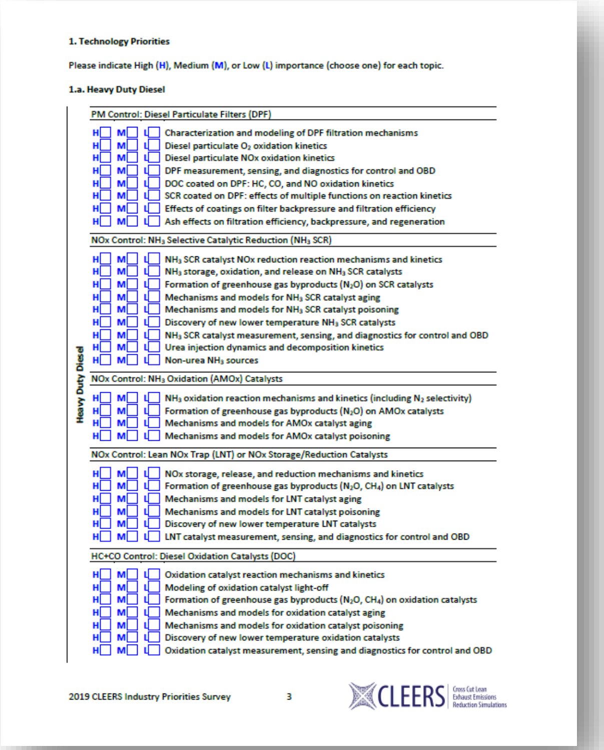
Pacific Northwest NATIONAL LABORATORY

*= collaborations with PNNL

Milestones

FY	Qtr	Milestone	Status
2019	4	Publish/present model for NO adsorption and release on a Pd-zeolite PNA	Complete
2019	4	Organize 2019 CLEERS Workshop	Complete
2020	2	Complete measurements of HC adsorption isotherms on a zeolite-based HC trap	Complete
2020	4	Organize 2020 CLEERS Workshop	On schedule
2021	2	Publish/present a model for HC adsorption and release on a HC trap	On schedule
2021	4	Organize 2021 CLEERS Workshop	On schedule

2019 CLEERS Industry Priorities Survey shows participants still value many of the CLEERS organization activities, especially the workshop and teleconferences



1. Technology Priorities

Please indicate High (H), Medium (M), or Low (L) importance (choose one) for each topic.

1.a. Heavy Duty Diesel

Heavy Duty Diesel

PM Control: Diesel Particulate Filters (DPF)

- H☐ M☐ L☐ Characterization and modeling of DPF filtration mechanisms
- H☐ M☐ L☐ Diesel particulate O_2 oxidation kinetics
- H☐ M☐ L☐ Diesel particulate NOx oxidation kinetics
- H☐ M☐ L☐ DPF measurement, sensing, and diagnostics for control and OBD
- H☐ M☐ L☐ DOC coated on DPF: HC, CO, and NO oxidation kinetics
- H☐ M☐ L☐ SCR coated on DPF: effects of multiple functions on reaction kinetics
- H☐ M☐ L☐ Effects of coatings on filter backpressure and filtration efficiency
- H☐ M☐ L☐ Ash effects on filtration efficiency, backpressure, and regeneration

NOx Control: NH_3 Selective Catalytic Reduction (NH_3 SCR)

- H☐ M☐ L☐ NH_3 SCR catalyst NOx reduction reaction mechanisms and kinetics
- H☐ M☐ L☐ NH_3 storage, oxidation, and release on NH_3 SCR catalysts
- H☐ M☐ L☐ Formation of greenhouse gas byproducts (N_2O) on SCR catalysts
- H☐ M☐ L☐ Mechanisms and models for NH_3 SCR catalyst aging
- H☐ M☐ L☐ Mechanisms and models for NH_3 SCR catalyst poisoning
- H☐ M☐ L☐ Discovery of new lower temperature NH_3 SCR catalysts
- H☐ M☐ L☐ NH_3 SCR catalyst measurement, sensing, and diagnostics for control and OBD
- H☐ M☐ L☐ Urea injection dynamics and decomposition kinetics
- H☐ M☐ L☐ Non-urea NH_3 sources

NOx Control: NH_3 Oxidation (AMOx) Catalysts

- H☐ M☐ L☐ NH_3 oxidation reaction mechanisms and kinetics (including N_2 selectivity)
- H☐ M☐ L☐ Formation of greenhouse gas byproducts (N_2O) on AMOx catalysts
- H☐ M☐ L☐ Mechanisms and models for AMOx catalyst aging
- H☐ M☐ L☐ Mechanisms and models for AMOx catalyst poisoning

NOx Control: Lean NOx Trap (LNT) or NOx Storage/Reduction Catalysts

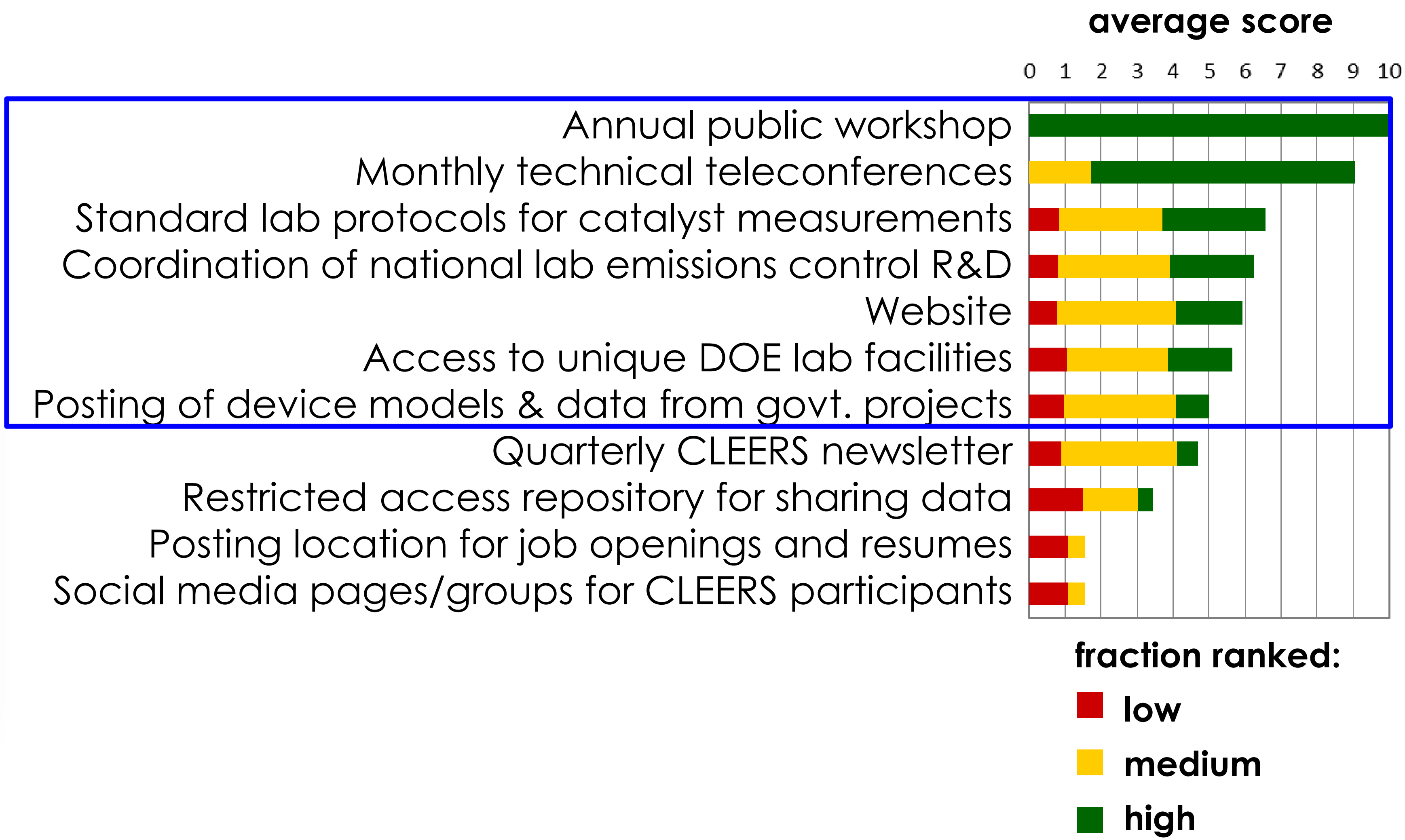
- H☐ M☐ L☐ NOx storage, release, and reduction mechanisms and kinetics
- H☐ M☐ L☐ Formation of greenhouse gas byproducts (N_2O, CH_4) on LNT catalysts
- H☐ M☐ L☐ Mechanisms and models for LNT catalyst aging
- H☐ M☐ L☐ Mechanisms and models for LNT catalyst poisoning
- H☐ M☐ L☐ Discovery of new lower temperature LNT catalysts
- H☐ M☐ L☐ LNT catalyst measurement, sensing, and diagnostics for control and OBD

HC+CO Control: Diesel Oxidation Catalysts (DOC)

- H☐ M☐ L☐ Oxidation catalyst reaction mechanisms and kinetics
- H☐ M☐ L☐ Modeling of oxidation catalyst light-off
- H☐ M☐ L☐ Formation of greenhouse gas byproducts (N_2O, CH_4) on oxidation catalysts
- H☐ M☐ L☐ Mechanisms and models for oxidation catalyst aging
- H☐ M☐ L☐ Mechanisms and models for oxidation catalyst poisoning
- H☐ M☐ L☐ Discovery of new lower temperature oxidation catalysts
- H☐ M☐ L☐ Oxidation catalyst measurement, sensing and diagnostics for control and OBD

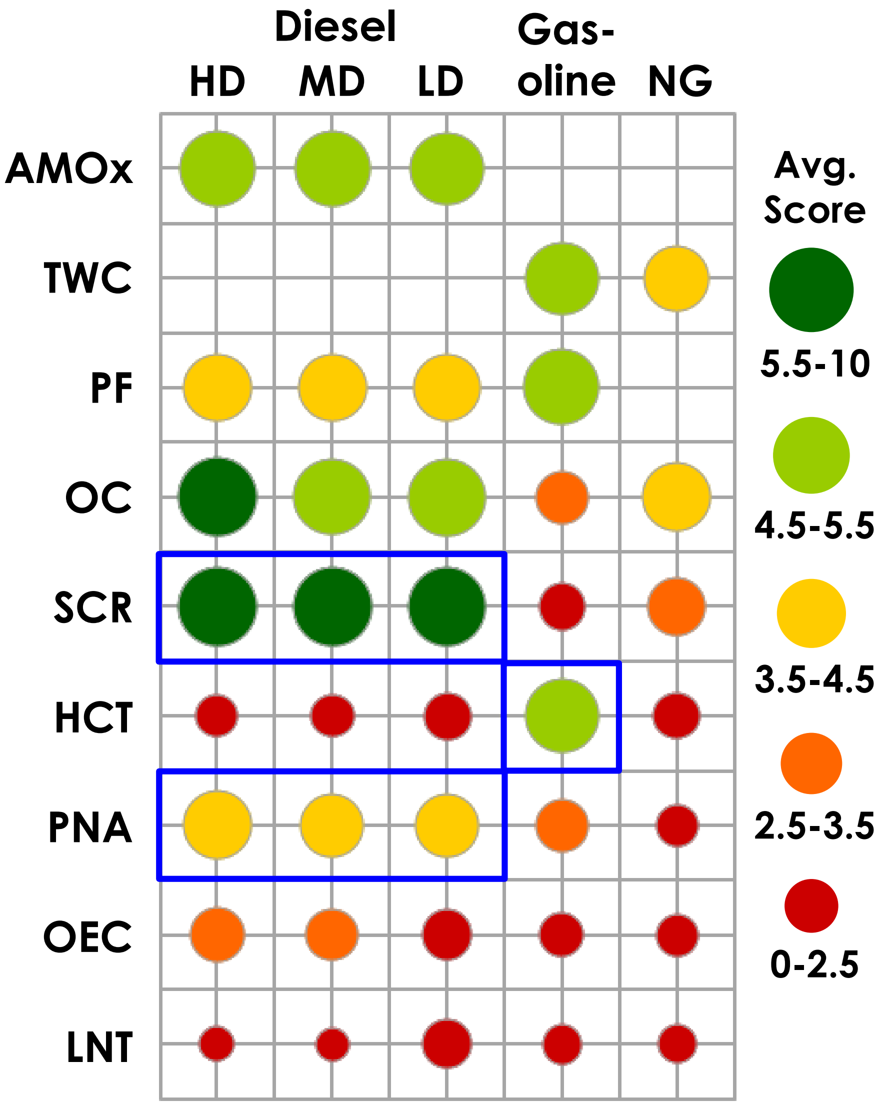
2019 CLEERS Industry Priorities Survey 3

CLEERS Cross Cut Lean Exhaust Emissions Reduction Simulations



2019 CLEERS Industry Priorities Survey results provide insights on R&D needs and guide ORNL CLEERS activities

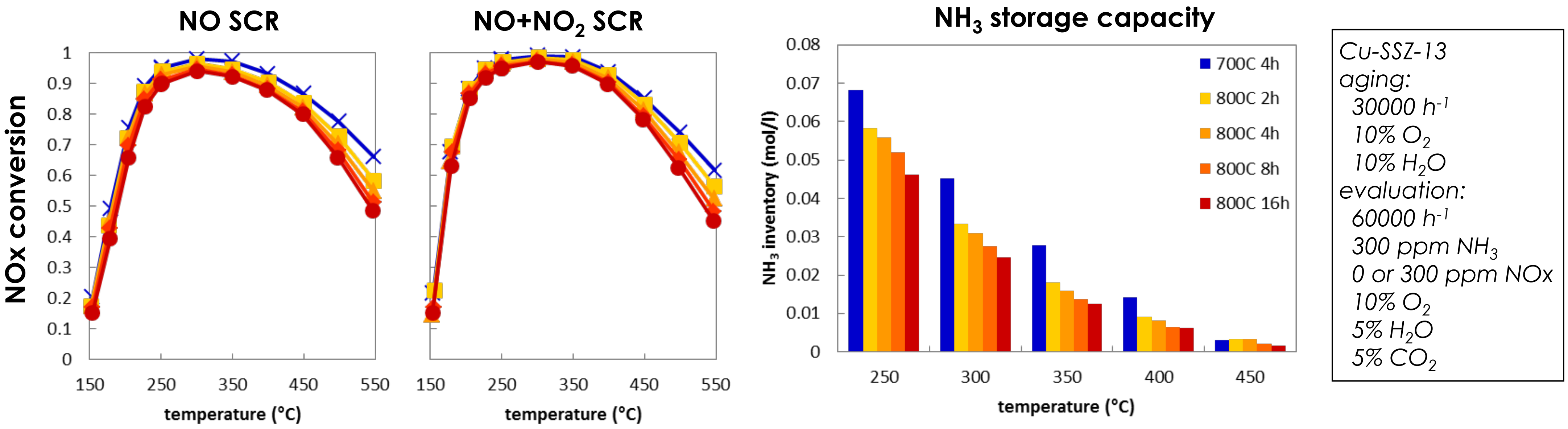
- Plot represents averaged scores across all topics within each technology separated by sector
- Top technologies by sector:
  - Diesel: SCR, DOC, AMOx
  - Gasoline: TWC, GPF, HCT
  - Natural gas: TWC, MOC
- Several notable shifts since 2017:
  - TWC up
  - PNA down
  - LNT down



- Survey results guide ORNL CLEERS Kinetics activities
- SCR: highest ranked technology for diesel
  - SCR aging: #3 topic across all HDD technologies & topics
  - Re-started modeling of aging effects on SCR
- HCT: second highest ranked technology for gasoline
  - Ramped up work on HCT adsorption/desorption
- PNA: highest ranked technology in 2017, but interest has waned since
  - Ramped down PNA work

SCR: Modeling of aging impacts on Cu-SSZ-13 SCR catalyst performance

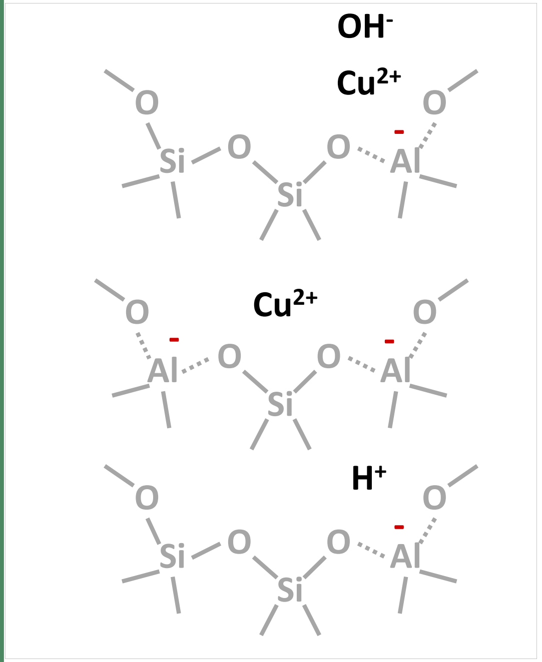
- Prior work (FY2015-2017) focused on hydrothermal aging of a commercial Cu-SSZ-13 (GM truck)
  - Observed largest impact was loss of high temperature NH_3 storage capacity
  - Collected enormous data set on NH_3 adsorption/desorption as a function of aging



- Future HD emissions regulations may increase durability requirements significantly (>800 k miles)
  - Hired (Jan. 2020) an expert on modeling of adsorption/desorption phenomena in zeolites
  - Developing strategies for modeling changes in catalyst performance over vehicle full useful life by starting with prior data sets on aging of Cu-SSZ-13

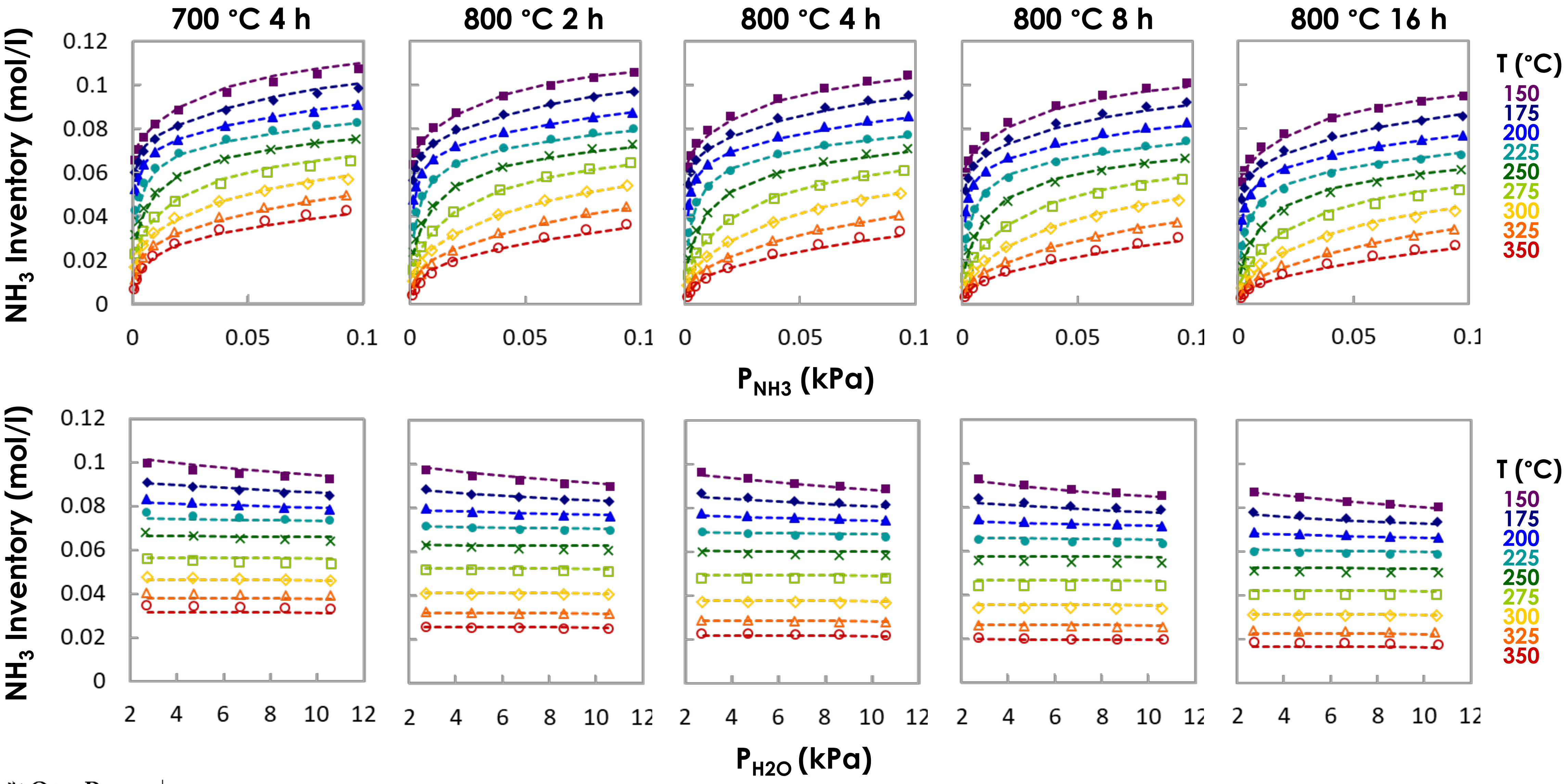
SCR: Model development initially focused on how aging impacts NH_3 storage

- Model formulation based on thermodynamics of NH_3 and H_2O adsorption calculated at numerous potential sites in Cu-SSZ-13 (Paolucci et al., JACS, 138 (2016) 6028-6048)
- Model includes 3 distinct NH_3 storage sites with constant adsorption enthalpies (Langmuir isotherm)
  - One site includes H_2O competition
- Adsorption energetic parameters and site densities were fit to NH_3 storage data sets
  - Only site densities were varied with aging

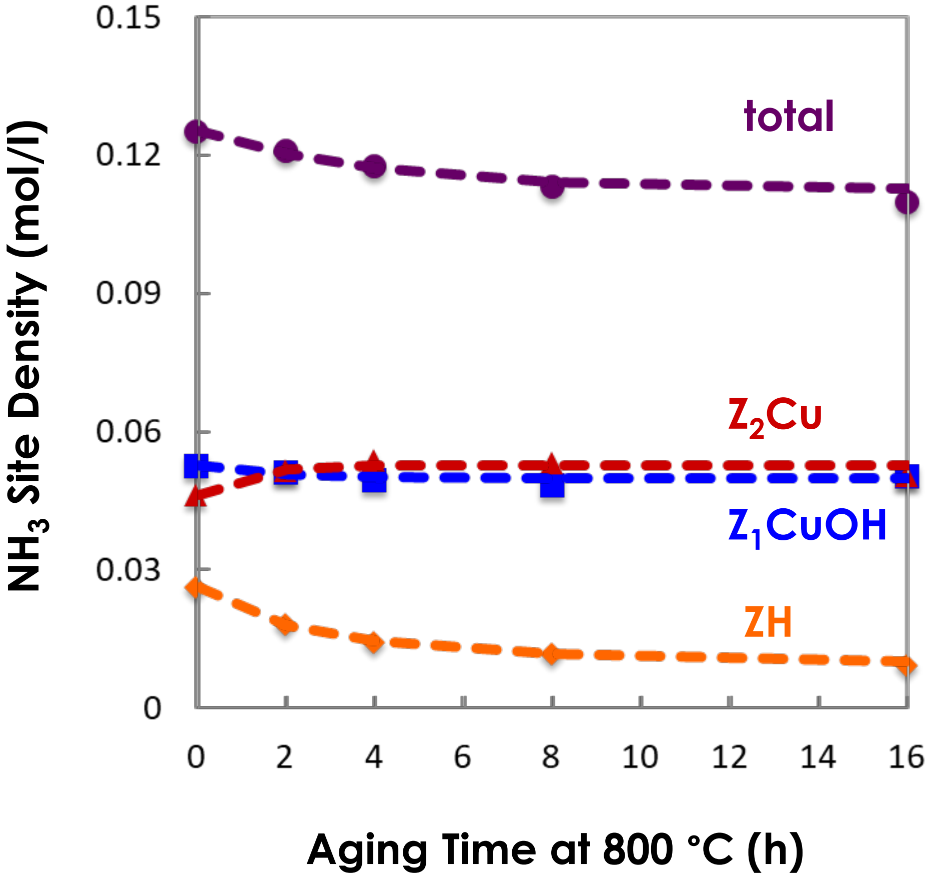


Adsorption Reaction	Inventory Expression	ΔH (kJ/mol)	ΔS (J/K/mol)
$Z_1CuOH + NH_3 \leftrightarrow Z_1CuOH\text{-}NH_3$ $Z_1CuOH + H_2O \leftrightarrow Z_1CuOH\text{-}H_2O$	$w_1\left(\frac{K_1 C_{NH_3}}{1 + K_1 C_{NH_3} + K_4 C_{H_2O}}\right)$	-54.5 -32.1	-30.0 -24.2
$Z_2Cu + NH_3 \leftrightarrow Z_2Cu\text{-}NH_3$	$w_2\left(\frac{K_2 C_{NH_3}}{1 + K_2 C_{NH_3}}\right)$	-78.1	-41.1
$ZH + NH_3 \leftrightarrow ZH\text{-}NH_3$	$w_3\left(\frac{K_3 C_{NH_3}}{1 + K_3 C_{NH_3}}\right)$	-91.9	-28.9

SCR: NH_3 storage model accurately predicts NH_3 inventories over a wide range of temperatures and compositions; aging is captured by changing only site densities



SCR: Kinetic model for conversion of NH_3 storage sites with aging captures changes in site densities calculated from NH_3 storage isotherm data sets

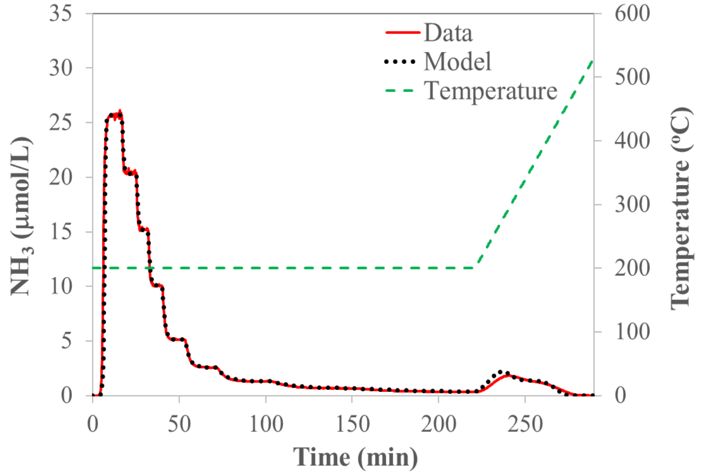


- Developed aging model to predict changes in NH_3 storage site densities
- Fit aging kinetic parameters to calculated changes in site densities from adsorption isotherms
- Resulting aging kinetic model captures changes in site densities reasonably well

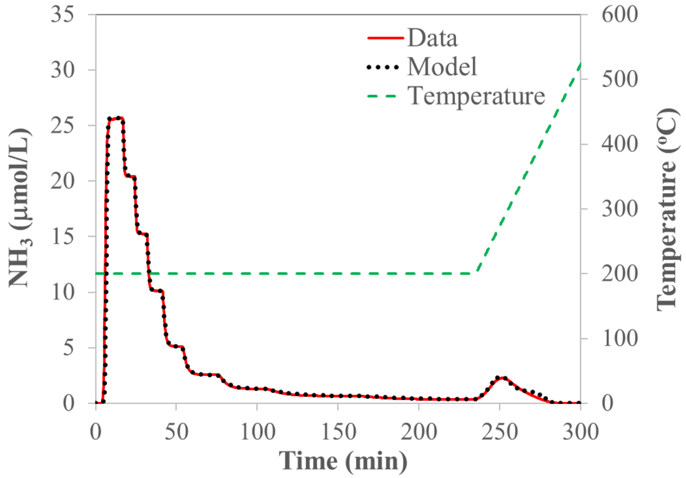
Aging Reaction	Rate Expression	k (h^{-1})
ZH + ZCu → Z_2Cu + H_2O	$\frac{d[\text{(ZH)(ZCu)}]}{dt} = -k_1[\text{(ZH)(ZCu)}]C_{O_2}^{0.25}$	k_1: 0.92
ZH + CuO ↔ Z_1CuOH	$\frac{d[Z_1\text{CuOH}]}{dt} = k_{-2}[\text{(ZH)(CuO)}] - k_2[Z_1\text{CuOH}]$	k_2: 0.10 k_{-2}:0.49
2ZH + $0.5O_2$ → 2Z	$\frac{d[\text{ZH}]}{dt} = -k_3[\text{ZH}]C_{O_2}^{0.25}$	k_3: 0.24

SCR: NH_3 storage model has been successfully converted to a transient kinetic scheme for NH_3 adsorption and desorption

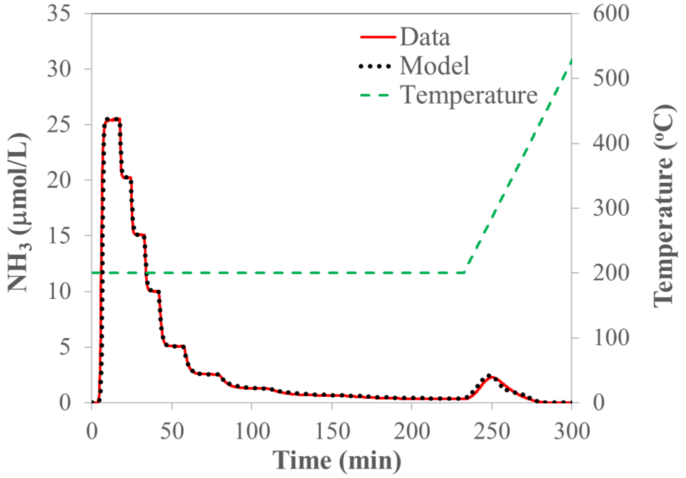
700 °C 4 h



800 °C 2 h

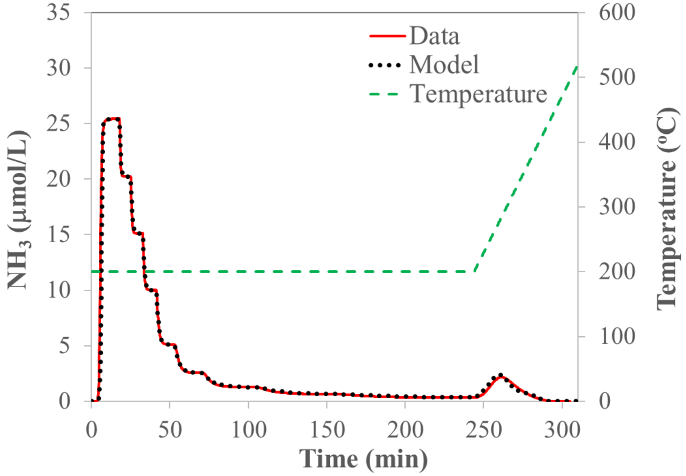


800 °C 4 h

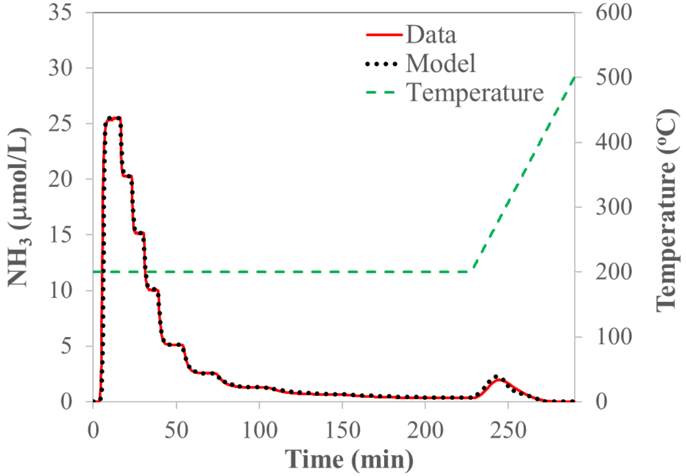


- Converted steady state NH_3 storage model into expressions for adsorption/desorption rates
- Resulting kinetic model accurately captures isothermal desorption data (Some TPD wrinkles remain)
- Next step: SCR reactions

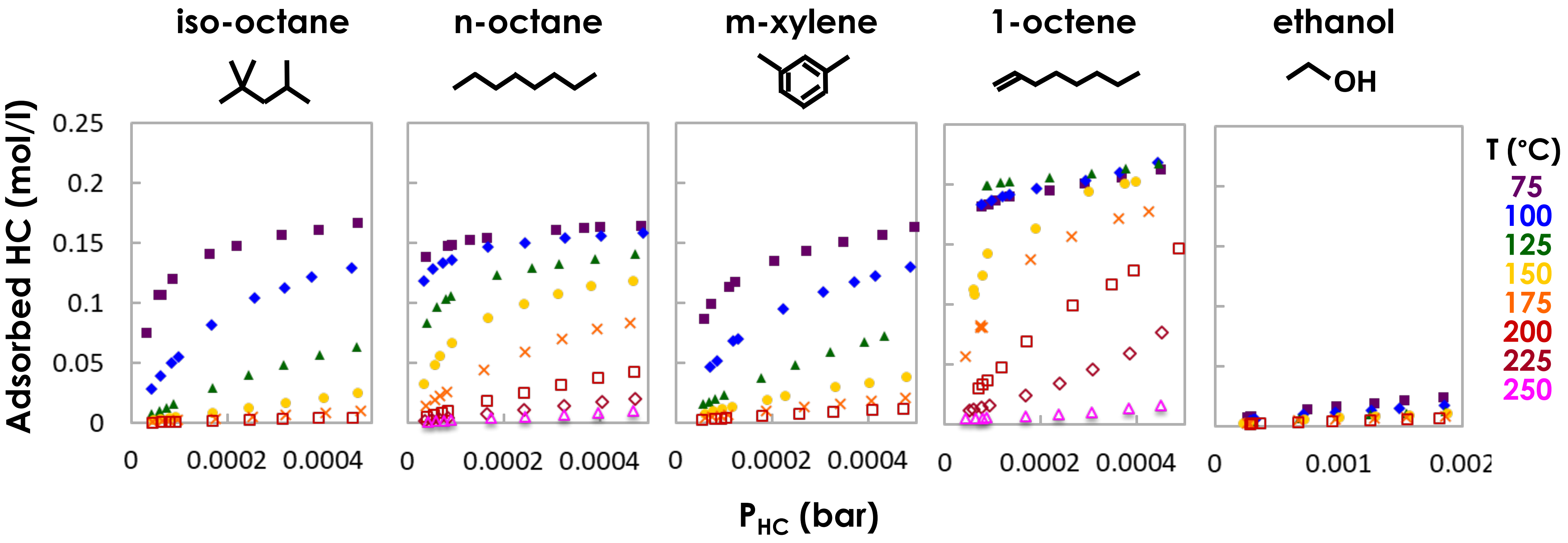
800 °C 8 h



800 °C 16 h



HCT: Chemical structure impacts storage isotherms on BEA zeolite trap material

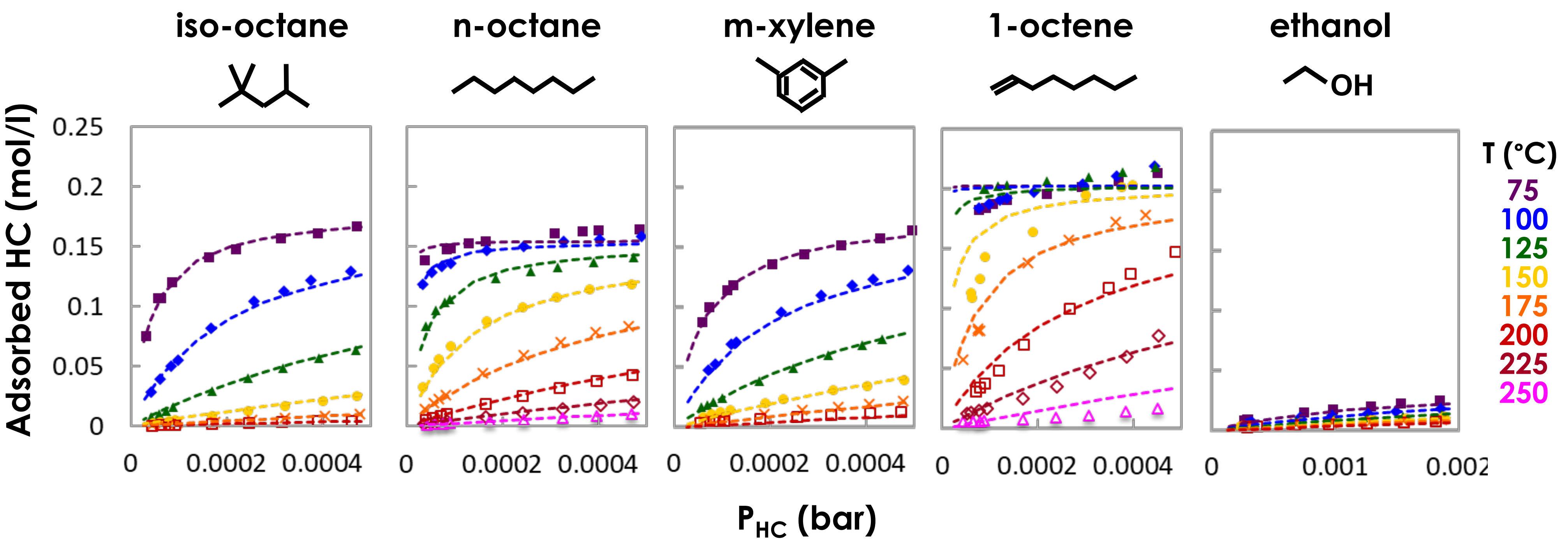


Extruded BEA zeolite (Johnson Matthey)

degreen: 700 °C 4 h
30000 h^{-1}
10% O_2
10% H_2O
10% CO_2
evaluate:
60000 h^{-1}
200-3000 ppm C1 HCs
0.5% O_2
13% H_2O
13% CO_2

- Experiments included a range of (mostly C8) chemical structures found in gasoline
  - Similar species are found in cold start gasoline engine exhaust (ACE153)
- Linear HCs have higher uptake than branched or aromatic HCs
- Higher uptake of 1-octene could in part be due to surface reactions (coke formation)
- Unexchanged BEA stores very little ethanol

HCT: Simple single site Langmuir isotherm captures storage capacity trends



Single-site Langmuir isotherm:

$$\omega_{HC} = \theta_{HC}\omega_{Total}$$

$$\theta_{HC} = \frac{K_{ads}\,p_{HC}}{1 + K_{ads}\,p_{HC}}$$

$$K_{ads} = e^{\left(\frac{-\Delta G_{ads}}{RT}\right)}$$

$$\Delta G_{ads} = \Delta H_{ads} - \Delta S_{ads} T$$

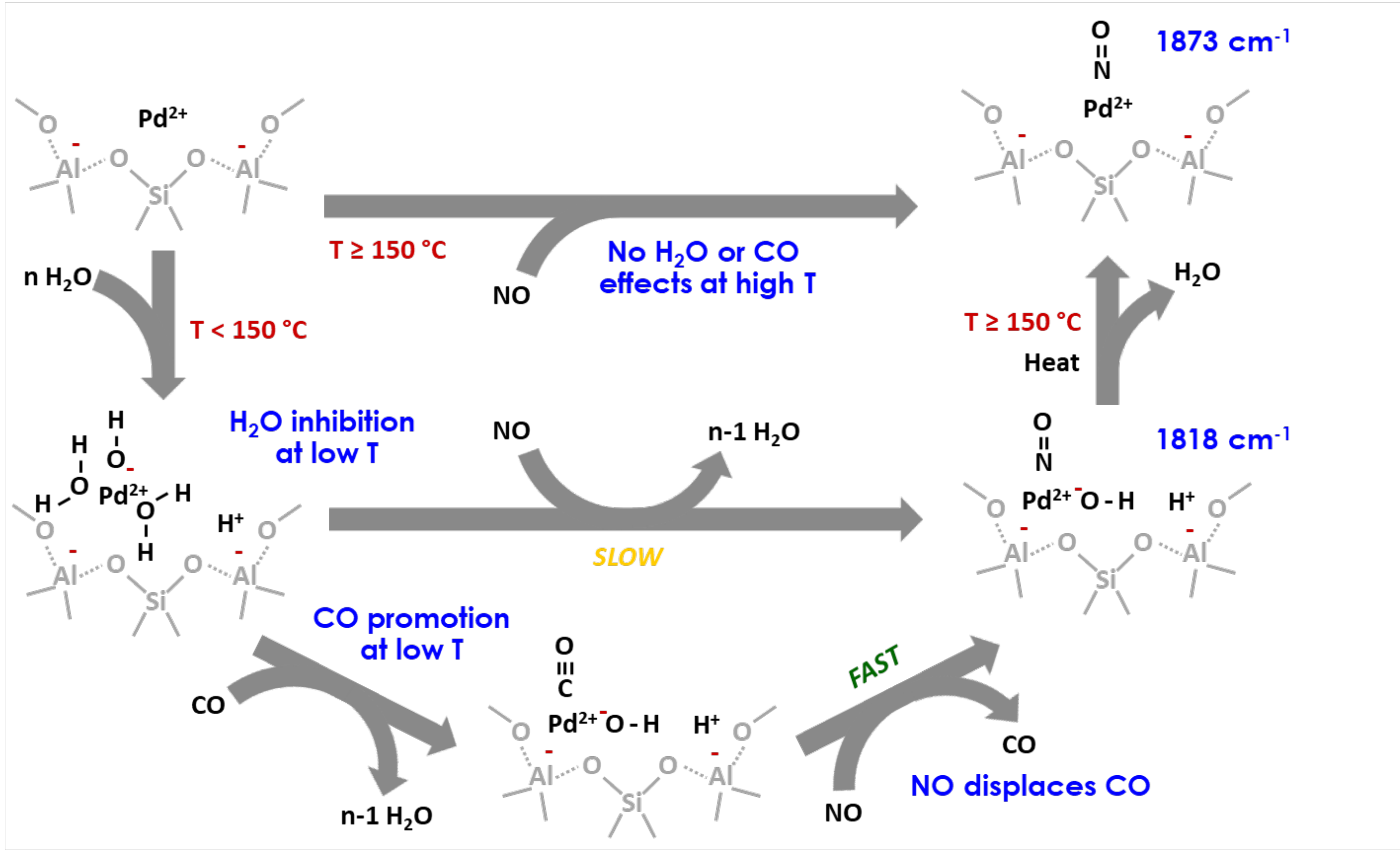
ω_{Total}	0.181	0.155	0.180	0.203	0.040	(mol/l)
ΔH_{ads}	-68500	-71100	-53000	-89000	-21200	(J/mol)
ΔS_{ads}	-113	-94	-72	-120	-6.3	(J/K/mol)

- Model discrepancies with 1-octene likely due to surface reactions
- Next steps: isotherms for blends, transient uptake/release experiments

PNA: Wrapping up mechanism development work, investigating capacity loss on sequential NO storage/release cycling with UVA

Collaboration with University of Virginia (Kevin Gu, Prof. William Epling)

- Writing manuscript on NO adsorption/desorption mechanisms
  - Pd-ZSM-5 model PNA material (from Johnson-Matthey)
- Investigating underlying cause of loss of NO storage capacity on sequential cycling in Pd-zeolites
  - UVA subcontract
  - UVA-synthesized materials
- Future PNA modeling work contingent upon discovery of a PNA material with stable adsorption capacity



Collaborations: 33 Industry, 23 Academic, 12 Natl. Labs/Govt.

CLEERS Participants

CLEERS Technology Focus Group

Advanced Engine Crosscut

ACEC Tech Team

U.S. Govt.:
DOE VTO

LD OEMs:
FCA
Ford
GM

EPA
TARDEC

CLEERS Industry Survey Recipients

HD OEMs:
Caterpillar
Cummins
Daimler
Navistar
Paccar
Volvo

Suppliers:
BASF
Johnson-Matthey
Umicore
Corning
Delphi

Industry:
John Deere
Bosch
Tenneco
IAV
Emissol

National Labs:
ORNL
PNNL
ANL
LANL

Universities:
Chalmers Univ.
Michigan Tech. Univ.
Pennsylvania State Univ.
Politecnico di Milano
Purdue Univ.
UCT Prague
Univ. of Houston
Univ. of Kentucky
Univ. of Notre Dame
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Mass. Inst. of Tech.
Queens Univ. Belfast
Seoul National Univ.

SUNY at Buffalo
Univ. of Connecticut
Univ. of Mass. Amherst
Univ. of New Mexico
Univ. of Tennessee

Responses to Comments from Reviewers

Reviewer Comments:	Responses:
• *"Perhaps the greatest challenge today for palladium (Pd)/zeolite PNAs is the gradual deterioration of the storage efficiency on back-to-back tests."*	• Remaining PNA work focused on capacity degradation, primarily through UVA subcontract • PNA modeling efforts have been put on hold until this problem has been resolved
• *"…the PNA work should focus on novel materials that are not part of another lab effort."*	• This project does not develop new materials • We develop models for promising materials that have been developed elsewhere • Other projects in the DOE VTO portfolio are addressing this issue (including tasks at PNNL and ORNL)
• *"Over the years, CLEERS has been flexible to redirect itself according to the shifting priorities in the field and industry, such as stronger focus on PNA and hydrocarbon traps. In the process, however, **a couple of focused activities—such as ammonia (NH3) storage—were sacrificed.** Given the project team's expertise, the reviewer recommended that the project receives more resources to tackle further challenges in broader sense; CLEERS is a worthwhile "bang for the buck."*	• We are trying to make the most of the resources we have by expanding our team through additional ORNL staff and outside collaborations • We have relaunched our NH_3 storage modeling efforts • We will continue working on low temperature traps, although PNA efforts are currently at a reduced level • We will continue to look for ways to make the most of our resources while being responsive to industry needs

Remaining Challenges & Barriers/Future Work

Remaining Challenges:	**Future Work:** *(subject to change based on funding)*
• Ongoing need for coordination and collaboration in emissions control R&D	• Continue coordinating CLEERS activities: workshops, teleconferences, website, surveys
• Future requirements for >800,000 mi full useful life for HD emissions control systems	• ***Urea SCR catalysts:*** - Develop full kinetic SCR model that incorporates effects of aging on NH_3 storage and NOx conversion performance
• Low exhaust temperatures from higher efficiency engines and advanced combustion modes • Cold start emissions compliance • 90% conversion of NOx and HCs at 150 °C	• ***Hydrocarbon traps:*** - Measure transient HC uptake over BEA zeolite sample - Develop transient kinetic models for HC trap storage/release - Measure adsorption isotherms over a Pd-ZSM-5 HC trap - Quantify effects of aging on HC uptake and release • ***Passive NOx Adsorbers:*** - Publish paper on Pd-ZSM-5 NO adsorption/desorption - Identify mechanism of NO storage capacity loss during repeated storage/release experiments (UVA subcontract)

Summary

- **Relevance**
  - CLEERS supports the development of simulation tools for the design, optimization, and control of next generation advanced combustion engine/aftertreatment systems that maximize efficiency while still meeting emissions standards
- **Approach**
  - Promote sharing of precompetitive information among the emissions control community through workshops, teleconferences, website, and surveys
  - Develop modeling strategies, reaction mechanisms, parameter estimates, experimental protocols, and data sets to support development of aftertreatment simulation tools, with a particular focus on catalysts for low temperature exhaust
- **Technical Accomplishments**
  - Maintained high levels of participation in CLEERS activities
  - Developed a detailed model that captures aging effects on NH_3 storage over Cu-SSZ-13
  - Measured adsorption isotherms for several gasoline constituents on a BEA zeolite hydrocarbon trap
- **Collaborations**
  - University of Virginia, Johnson Matthey, PNNL
  - Advanced Engine Crosscut Team, U.S.DRIVE ACEC Tech Team, CLEERS Participants
- **Future Work** *(subject to change based on funding levels)*
  - Continue coordination of CLEERS activities
  - Measure & model adsorption/desorption phenomena on PNAs, HC Traps, and urea SCR catalysts

Technical Backup Slides

Abbreviations

AMOx	Ammonia oxidation catalyst
CUC	Clean-up catalyst
DOC	Diesel oxidation catalyst
DPF	Diesel particulate filter
GOC	Gasoline oxidation catalyst
GPF	Gasoline particulate filter
HCT	Hydrocarbon trap
LNT	Lean NOx trap
MOC	Methane oxidation catalyst
OC	Oxidation catalyst
OEC	Other emissions control catalysts
PF	Particulate filter
PNA	Passive NOx adsorber
SCR	Selective catalytic reduction
TWC	Three-way catalyst

ACI	Advanced compression ignition
BTE	Break thermal efficiency
CDC	Conventional diesel combustion
HD	Heavy duty
LD	Light duty
LTAT	Low temperature aftertreatment
LTC	Low temperature combustion
MD	Medium duty
NG	Natural gas
SI	Spark ignition